

The fluorine effect on the stability of phosphalkenes, phosphasilenes, oxophosphane, thioxophosphane and their rearranged isomers

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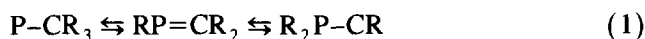
Abstract

Ab initio molecular orbital calculations at the QCISD(T)/6-311G(d,p)//(U)MP2/6-31G(d,p) + ZPE level have been applied to determine the relative energies between the species featuring double bond to phosphorus, $X_2C=PX$, $X_2Si=PX$, $XP=O$ and $XP=S$, and their rearranged products $XC-PX_2$, X_3C-P , $XSi-PX_2$, X_3Si-P , POX and PSX . The energy ordering between isomers is strongly dependent on the halogen substituents. When P is bonded to a more electronegative element, such as C, O and S, fluorination at P enormously stabilizes the corresponding species. The molecular stability is overwhelmingly dominated by the strength of the P–F bond. When P is bonded to a more electropositive element, such as Si, a reversal of role occurs. The relative stability is now mainly determined by the Si–F bond strength. Perfluorination amplifies the effect in such a way that in the $SiPX_3$ system, the P–SiF₃ phosphinidene turns out to be the most stable isomer, making it an attractive target for a laboratory preparation. While the negative hyperconjugation effect in some cases plays a noticeable effect, the ‘cis-effect’ is not operative. The effect of chlorine has also been examined in both XPO and XPS cases. The singlet–triplet energy separations were also estimated for the carbenes, silylenes and phosphinidenes involved.

Keywords: Molecular orbital calculations; Phosphorus; Silylene; Fluorine; Carbene; Phosphinidene

1. Introduction

The chemistry of dicoordinated phosphorus(III) compounds involving the $-P=C<$, $-P=N-$ and $-P=P-$ double bonds, is well documented in various review articles [1–3]. Several theoretical studies on these types of compound have also been performed [4–7]. Recently, experimental and theoretical investigations on the oxophosphanes ($-P=O$) and thioxophosphanes ($-P=S$) have also been reviewed [8]. Experimental structural data for phosphasilenes ($-P=Si<$) are rather scarce [9]. As yet, because the latter are highly soluble, only a few $-P=Si<$ compounds have been obtained in crystalline form. One of the most interesting features of these compounds is the existence of different low-lying isomers whose chemistries are also very rich. For example, phosphinocarbenes and alkylphosphinidenes, which are both observable isomers of phosphalkenes (Eq. (1)), are known to undergo typical reactions.



The relative energies between these isomers are, as

expected, strongly dependent upon the substituents. In some cases, a reverse energy ordering can be found. In recent papers [10,11], we have demonstrated that perfluorophosphinonitrene (F_2PN) is more stable by about 67 kJ mol^{-1} than its classical $FP=NF$ isomer, whereas an opposite ordering holds true for the unsubstituted and monohalogenated species. The main reason for such an energy reversal resides in the strength of the P–F bond, whose bond energy amounts to 552 kJ mol^{-1} in PF_3 [12]. The perfluorophosphinophosphinidene (F_2PP) has also been found to be markedly stabilized with respect to its $FP=PF$ isomer [11]. Recent theoretical studies [13,14] also pointed out some remarkable effects of halogen atoms, in particular fluorine, on the stabilities of phosphorus compounds.

Another effect of fluorine is better known as the ‘cis-effect’ [15,16] which exerts a larger stabilization of the cis-component of an $FA=BF$ molecule rendering the cis-conformer more stable than its trans counterpart. The cis-effect observed in $HFC=CHF$, $FN=NF$ and $FN=PF$ is believed to arise from a stabilizing $n(F) \rightarrow \sigma^*(F)$ interaction which is naturally more favourable in a cis-disposition of the two fluorine atoms. Nevertheless, such a behaviour no longer exists in $FP=PF$

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[11,17] where the trans-conformer is more stable than the cis.

In view of the results summarized above, it is of interest to have a larger survey of the effect of fluorine atoms on the thermodynamic stabilities of compounds containing a double bond to phosphorus and their isomers which is reflected in their relative energies. In the present paper, we report quantum chemical calculations on the model systems including phosphathenes $X_2C=PX$, oxophosphanes $O=PX$, phosphasilenes $X_2Si=PX$ and thioxophosphanes $S=PX$. We have considered the energy ordering of these compounds with respect to their isomers, being respectively the phosphino-substituted carbenes $XC-PX_2$ and alkylphosphinidenes $P-CX_3$, hydroxy-substituted phosphinidenes $P-OX$, phosphinosilylenes $XSi-PX_2$ and silylphosphinidenes $P-SiX_3$ and thiohydroxyphosphinidenes $P-SX$. While the effect of F has been considered for all systems, the effect of Cl has also been examined for both O and S systems.

We have further included in this investigation, calculations to estimate the singlet–triplet gaps of the carbenes, silylenes and phosphinidenes involved. The first and the last ones, normally have a triplet ground state but their electronic structure is, as would be expected,

strongly influenced by substituents. Note that the X_2PN and X_2P_2 species with $X = H, F$ and Cl have already been examined in detail in previous papers [10,11].

2. Details of calculation

Ab initio molecular orbital calculations were used to locate and characterize the equilibrium structures of interest by means of the GAUSSIAN 92 set of programs [18]. Geometry optimizations were uniformly performed at the (U)MP2/6-31G(d,p) level; the unrestricted formalism being employed for open-shell structures. A vibrational analysis was done at the (U)HF/6-31G(d,p) level to characterize the structures and thereby to estimate their zero-point vibrational energies (ZPEs) whose calculated values were scaled by 0.9. The final estimates for the relative energies are the results of single-point electronic energy calculations using the quadratic configuration interaction method and a larger basis set (U)QCISD(T)/6-311G(d,p) at (U)MP2-geometries and corrected for ZPE. Throughout this paper, bond lengths are given in angströms, bond angles in degrees, total energies in hartree, and zero-point and relative energies in kilojoules per mole.

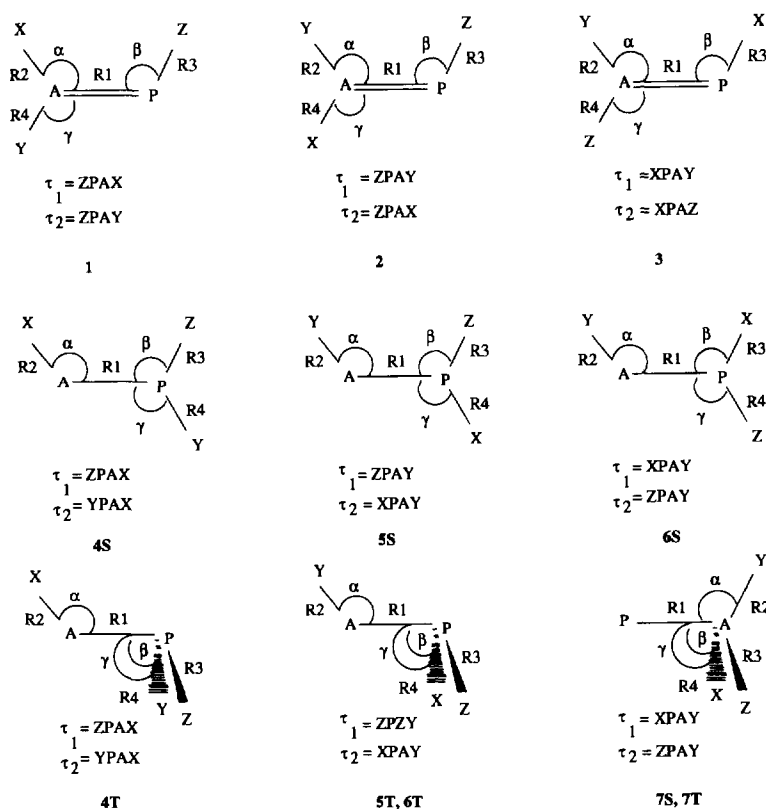


Fig. 1. Schematic representation of PAXYZ equilibrium structures with $A = C, Si$; $X, Y, Z = H, F$. While singlet carbenes and silylenes **4**, **5** and **6** are symbolized by the letter S, the letter T stands for their corresponding triplet states. Structures **7S** and **7T** are the isomeric phosphinidenes in both electronic states. R1, R2, R3, R4 are bond lengths, α , β , γ are bond angles and τ_1 , τ_2 symbolize dihedral angles.

3. Results and discussion

For each of the PXYZ systems considered in which A stands for C or Si and X,Y,Z stand for H and/or F, we have examined at most seven singlet structures denoted by **S** and three triplet structures denoted by **T** shown in Fig. 1. While structures **1**, **2** and **3** represent the *Z* and *E* isomeric forms of $\text{XYA}=\text{PZ}$, structures **4**, **5** and **6** represent the phosphinocarbenes and phosphinosilylenes YA-PXZ . Structures **7** correspond to either methyl or silylphosphinidene derivatives. In many cases, differently labelled structures become identical, for example **5T** and **6T**. For PCXYZ the (U)MP2/6-31G(d,p) optimized geometries are recorded in Table 1 and the corresponding total, zero-point and relative energies are summarized in Table 2. For PSiXYZ the (U)MP2/6-31G(d,p) optimized geometries are recorded in Table 3 and the corresponding total, zero-point and relative energies in Table 4. Schematic potential energy correlation diagrams illustrating the effect of fluorine atoms in PCXYZ and PSiXYZ are displayed in Figs. 2–4. The doubly bonded molecules **1** are used as energy references. It should, however, be stressed that the structure numbering is rather arbitrary; the same numbers in two systems do not necessarily correspond to comparable

isomers. Note that we have not considered the transition structures connecting the different isomers. The 1,2-H shifts in both (PCH_3) and (PSiH_3) systems have been examined in detail in earlier studies [4,19]. The 1,2-shift of fluorine is often more difficult to achieve than that of hydrogen.

3.1. The PCXYZ isomers

3.1.1. PCH_3 isomers

A 1,2-H shift in $\text{H}_2\text{C}=\text{PH}$ **1** in either the $\text{C} \rightarrow \text{P}$ or the $\text{P} \rightarrow \text{C}$ direction results in a stable isomer, with methylphosphinidene $\text{P}-\text{CH}_3$ **7S** being more stable than phosphinocarbene $\text{HC}-\text{PH}_2$ **4S**. While the latter carbene has a singlet ground state, the triplet state is more favoured in methylphosphinidene. The singlet–triplet energy separations, symbolized by $\Delta E(\text{T}-\text{S})$, amount to 33 kJ mol^{-1} in $\text{HC}-\text{PH}_2$ and -124 kJ mol^{-1} in $\text{P}-\text{CH}_3$ (as a convention, a negative value for $\Delta E(\text{T}-\text{S})$ corresponds to a triplet ground state). We note that singlet $\text{P}-\text{CH}_3$ has been investigated by different authors [4,31,32]. In particular, Schaefer and coworkers [32] have used two-configuration wavefunctions (TCSCF) for geometry optimization that result in smaller geometrical distortions than what we have calculated. It is probable that the larger distortion in **7S** arises from a

Table 1
(U)MP2/6-31G(d,p) optimized geometries of the PCXYZ isomers with X, Y, Z = H and/or F

System	Structure ^a	R1 (Å)	R2 (Å)	R3 (Å)	R4 (Å)	α (deg)	β (deg)	γ (deg)	τ_1 (deg)	τ_2 (deg)
PCH_3	1	1.675	1.085	1.422	1.081	124.8	97.0	116.0	0.0	180.0
	4S	1.624	1.090	1.410	1.383	115.5	137.8	117.0	0.0	180.0
	4T	1.776	1.079	1.408	1.408	131.7	99.4	99.4	-131.4	131.4
	7S	1.815	1.108	1.088	1.088	96.5	117.1	117.1	111.8	-111.8
	7T	1.855	1.089	1.089	1.089	110.8	110.8	110.8	120.0	-120.0
PCH_2F (X = F; Y,Z = H)	1	1.680	1.084	1.409	1.348	125.7	93.7	122.9	0.0	180.0
	2	1.681	1.083	1.408	1.349	127.6	91.4	111.4	0.0	180.0
	3	1.654	1.081	1.624	1.081	124.1	103.4	117.9	0.0	180.0
	4S	1.825	1.336	1.404	1.397	107.3	104.2	97.3	40.7	143.7
	4T	1.803	1.334	1.406	1.406	122.9	98.2	98.2	131.8	-131.8
	6S	1.569	1.077	1.626	1.378	123.2	143.5	117.6	0.0	180.0
	6T	1.766	1.078	1.407	1.627	133.1	95.5	103.2	203.1	103.0
	7S	1.795	1.401	1.099	1.099	118.0	107.9	107.9	123.0	-123.0
7T	1.868	1.399	1.092	1.092	110.0	110.8	110.8	119.7	-119.7	
PCHF_2 (X = H; Y,Z = F)	1	1.678	1.084	1.628	1.350	126.0	98.4	120.1	0.0	180.0
	2	1.674	1.344	1.621	1.086	126.3	102.0	119.9	0.0	180.0
	3	1.692	1.329	1.406	1.330	128.2	91.0	108.9	0.0	180.0
	4S	1.577	1.080	1.608	1.578	124.2	148.5	116.9	0.0	180.0
	4T	1.773	1.078	1.609	1.609	133.8	99.6	99.6	130.0	-130.0
	5S	1.774	1.319	1.626	1.404	119.7	116.0	88.3	22.6	124.4
	5T	1.790	1.325	1.624	1.404	123.8	103.9	92.0	99.4	-161.5
	6S	1.846	1.333	1.410	1.616	102.2	89.6	99.4	69.8	169.8
	7S	1.811	1.459	1.086	1.351	79.1	124.4	121.8	103.1	-104.8
7T	1.876	1.082	1.345	1.345	112.9	110.2	110.2	120.8	-120.8	
PCF_3	1	1.692	1.322	1.626	1.330	127.6	98.3	111.3	0.0	180.0
	4S	1.886	1.320	1.610	1.606	104.8	99.5	95.3	42.1	142.6
	4T	1.810	1.323	1.604	1.604	121.8	98.7	98.7	130.1	-130.1
	7S	1.830	1.399	1.343	1.399	90.4	120.7	120.7	111.2	-111.2
	7T	1.886	1.353	1.353	1.353	111.5	111.5	111.5	120.0	-120.0

^a See Fig. 1 for definitions of structures and parameters.

Table 2
Total and relative energies at the QCISD(T)/6-311G(d,p) level; relative energies are corrected for ZPEs

System	Structure ^a	Total energy ^b (a.u.)	ZPE ^c (kJ mol ⁻¹)	Relative energy (kJ mol ⁻¹)
PCH ₃	1	-380.63231	85	0
	4S	-380.53748	73	237
	4T	-380.52451	72	270
	7S	-380.56077	89	192
	7T	-380.60859	91	68
PCH ₂ F (X = F; Y,Z = H)	1	-479.69863	69	0
	2	-479.69880	69	0
	3	-479.73435	72	-91
	4S	-479.61155	58	217
	4T	-479.59409	57	262
	6S	-479.64590	58	127
	6T	-479.61916	60	200
	7S	-479.62584	72	194
	7T	-479.66594	75	92
PCHF ₂ (X = H; Y,Z = F)	1	-578.79017	54	0
	2	-578.78988	55	0
	3	-578.77617	51	34
	4S	-578.73203	44	143
	4T	-578.72970	44	149
	5S	-578.70215	45	222
	5T (= 6T)	-578.69111	46	252
	6S	-578.69814	45	233
	7S	-578.69151	56	261
	7T	-578.74450	58	124
	PCF ₃	1	-677.86258	36
4S		-677.79873	29	161
4T		-677.79895	30	161
7S		-677.78269	37	211
7T		-677.83534	38	73

^a See Fig. 1 for definitions of structures and parameters.

^b Based on (U)MP2/6-31G(d,p) geometries given in Table 1.

^c From (U)HF/6-31G(d,p) calculations and scaled by 0.9.

shortcoming of single-reference MP2 calculations. Concerning the energy, we wish, however, to refer to our recent article in which we have shown that the singlet-triplet energy separation in P-CH₃ is not much affected in using either high level mono-reference or multi-reference wavefunctions, when the basis set employed is large enough [33].

3.1.2. PCH₂F isomers

For the monofluorinated phosphathenes, three distinct geometrical isomers can be formed, namely *E*-HFC=PH **1**, *Z*-HFC=PH **2** and H₂C=PF **3**. Structures **1** and **2** are identical in energy and about 91 kJ mol⁻¹ higher in energy than structure **3**. The reason for this large energy gap can be found in the difference between both CF and PF bond energies, which amount to about 485 kJ mol⁻¹ and 552 kJ mol⁻¹ respectively [20,21]. The peculiar strength of the P-F bond has been analysed in detail in earlier papers [11,22]. A rapid look at Table 1 reveals that there is no particular change in the C=P bond of either **1** or **2**, whereas in **3** there is a shortening of 0.026 Å relative to the parent species. H₂C=PF **3** has been generated and characterized by microwave spec-

troscopy [23]. We note that the rotational constants of **3** derived from the MP2/6-31G(d,p) geometry compare reasonably with the experimental values:

Calculated	A _e = 27 496	Experimental	A _o = 28 483
(MHz):	B _e = 8790	(MHz):	B _o = 8890
	C _e = 6661		C _o = 6760

Isomerization of **1** and **2** with migration of either the hydrogen or the fluorine atom at carbon results in the carbenes **4S**, **5S** and **6S**. The form **5S** does not exist as a local minimum. Optimization for **5S** at the MP2 level invariably leads to **6S** which is the only HC-PHF structure. It is beyond doubt that FC-PH₂ **4S** is energetically less favoured than **6S**, because of its weaker C-F bond. Here, the difference also amounts to 90 kJ mol⁻¹. Nevertheless, the carbene **6S** lies 127 kJ mol⁻¹ above **1** and 218 kJ mol⁻¹ above **3**. Thus the smallest energy gap between a phosphathene and a phosphinocarbene is reduced by 19 kJ mol⁻¹ upon F-substitution at P. This apparently arises from a stabilization of the carbene which is well reflected in its shorter C-P distance. The overlap between the phosphorus lone-pair with the carbene empty p-orbital is enhanced by an F back-dona-

tion. The C–P distance of 1.569 Å in **6S** in fact constitutes the shortest C–P bond of the entire series. It is closer to that of a triple bond (1.542 Å in HC≡P) than a double bond (1.675 Å in H₂C=PH). This seems to make the phosphorus atom in **6S** have a certain pentavalent character approaching an alkylidynephosphorane structure, HC≡PHF. However, the HCP bond angle remains normally bent (123°).

Concerning the phosphinidene P–CH₂F **7S** and **7T**, the triplet remains the lower lying state, but $\Delta E(T - S)$ is now reduced by 22 kJ mol⁻¹ compared with the unsubstituted system. Relative to **3**, the phosphinidene form is, however, destabilized by 115 kJ mol⁻¹.

3.1.3. PCHF₂ isomers

The difluorinated phosphathene also exists in three conformations: the 1,2-substituted *E*-FHC=PF **1**, *Z*-FHC=PF **2** and the geminal 1,1-substituted F₂C=PH **3**. The latter is the least stable, lying 34 kJ mol⁻¹ above **1** and **2** which have the same energetic content. These results are interesting in at least two aspects:

(i) the *cis*-effect is no longer operative in phosphathenes. The C–P distance seems to be long enough to prevent the F-orbitals from overlapping;

(ii) the situation is in clear contrast with that in difluoroethenes, where the geminal 1,1-F₂C=CH₂ is more stable than the *cis*-1,2-FHC=CHF [24]. This points again toward the dominant role of the P–F bond. As evidenced by the longer C–F distances in **3**, a negative hyperconjugation is being put into effect which partly contributes to reduce the energy gap from 91 kJ mol⁻¹ in the monofluorinated species to 34 kJ mol⁻¹ in this case.

Of course, hyperconjugation is not the main factor responsible for such a reduction. While a 1,2 F-shift from the carbon atom in **1** and **3** results in the carbenes **4S** and **6S**, an H-shift in **2** gives the carbene **5S**. Of these three carbenic structures, HC–PF₂ **4S** is the most favoured one, lying 143 kJ mol⁻¹ above **1**. The relative ordering for **5S** and **6S** of FC–PHF is intriguing. The *Z*-isomer **5S** is 11 kJ mol⁻¹ more stable than the *E*-**6S**. However, this is not due to a *cis*-effect because the C–P distance is quite long (1.774 Å). This comes presumably from a delocalization of the C lone-pair into the σ^* (PF) bond in anti periplanar position which enables the electrons to delocalize in ‘straight lines’. That is a manifestation of an anomeric effect or a stereoelectronic effect. The geometric parameters of **5S** and **6S** indeed indicate

Table 3
(U)MP2/6-31G(d,p) optimized geometries of PSiXYZ isomers with X, Y, Z = H and/or F

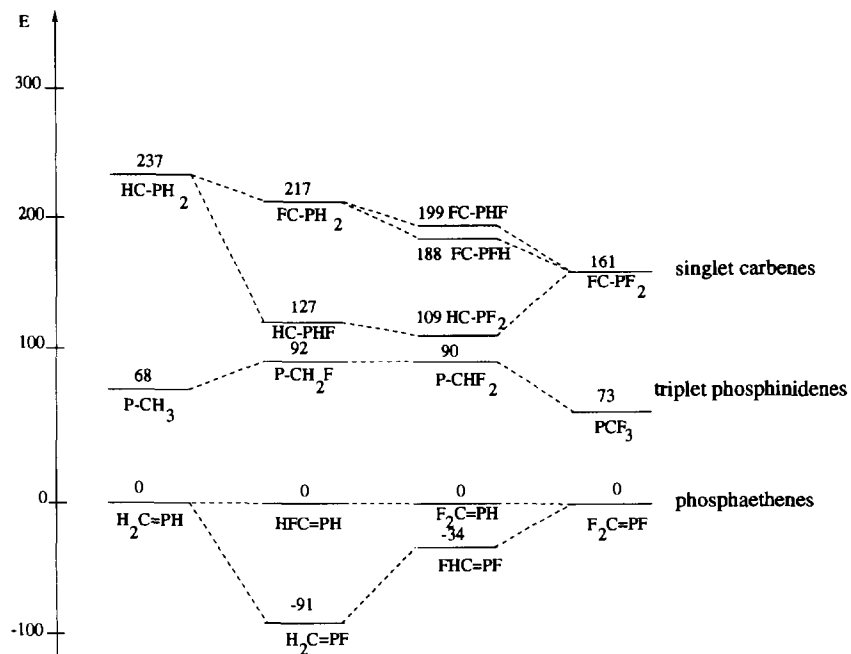
System	Structure ^a	R1 (Å)	R2 (Å)	R3 (Å)	R4 (Å)	α (deg)	β (deg)	γ (deg)	$\tau 1$ (deg)	$\tau 2$ (deg)	
PSiH ₃	1	2.078	1.413	1.471	1.471	123.9	89.3	123.9	0.0	180.0	
	4S	2.182	1.509	1.396	1.396	89.0	116.7	112.7	36.5	-205.0	
	4T	2.241	1.478	1.405	1.405	115.1	99.5	99.5	131.5	-131.5	
	7S	2.236	1.484	1.476	1.476	98.2	115.2	115.2	116.4	-116.4	
	7T	2.262	1.476	1.476	1.476	109.9	110.1	110.1	120.0	120.0	
	PSiH ₂ F (X = F; Y, Z = H)	1	2.050	1.585	1.409	1.463	126.8	93.0	126.0	0.0	180.0
		2	2.056	1.470	1.418	1.613	129.4	83.2	123.9	0.0	180.0
3		2.103	1.470	1.643	1.470	127.9	101.1	116.5	0.0	180.0	
4S		2.270	1.631	1.404	1.404	98.2	101.0	99.8	46.0	146.7	
4T		2.257	1.632	1.405	1.405	114.8	99.4	99.4	131.6	-131.6	
5S		2.083	1.529	1.392	1.615	71.0	130.1	128.4	0.0	180.0	
5T		2.242	1.481	1.634	1.409	114.8	105.1	95.0	156.2	-103.5	
6S		2.094	1.508	1.615	1.391	86.4	131.2	126.6	0.0	180.0	
7S		2.211	1.598	1.464	1.464	112.4	103.3	103.2	116.0	-116.0	
7T		2.252	1.621	1.474	1.474	110.6	109.8	109.8	119.5	-119.9	
PSiHF ₂ (X = H; Y, Z = H)	1	2.096	1.469	1.659	1.615	128.7	94.2	121.2	0.0	180.0	
	2	2.094	1.612	1.643	1.469	130.2	110.4	119.4	0.0	180.0	
	3	2.055	1.601	1.415	1.601	127.2	84.2	127.2	0.0	180.0	
	4S	2.300	1.510	1.626	1.626	87.2	100.6	100.6	58.2	158.8	
	4T	2.276	1.484	1.613	1.613	109.8	101.9	101.9	129.8	-129.8	
	5S	2.292	1.626	1.638	1.415	99.5	104.8	91.9	24.3	125.6	
	5T	2.257	1.630	1.630	1.410	114.8	106.6	91.4	-101.4	159.0	
	6S	2.298	1.634	1.415	1.645	94.6	91.7	98.4	67.0	167.0	
	7S	2.226	1.466	1.610	1.610	119.4	106.8	106.8	120.5	-120.8	
	7T	2.244	1.468	1.609	1.609	113.0	109.9	109.9	121.0	-121.0	
PSiF ₃	1	2.100	1.600	1.654	1.600	125.9	95.2	95.2	0.0	180.0	
	4S	2.346	1.628	1.638	1.638	99.3	89.8	89.8	102.1	201.1	
	4T	2.326	1.633	1.607	1.607	106.8	102.0	102.0	130.3	-130.3	
	7S	2.207	1.600	1.600	1.600	102.8	115.7	115.7	118.6	-118.6	
	7T	2.233	1.599	1.599	1.599	111.4	111.4	111.4	120.0	-120.0	

^a See Fig. 1 for definitions of structures and parameters.

Table 4

Total and relative energies at the QCISD(T)/6-311G(d,p) level of the PSiXYZ systems considered; relative energies are corrected for ZPEs

System	Structure ^a	Total energy ^b (a.u.)	ZPE ^c (kJ mol ⁻¹)	Relative energy (kJ mol ⁻¹)
PSiH ₃	1	-631.64303	63	0
	4S	-631.62028	62	59
	4T	-631.58733	62	145
	7S	-631.57305	62	183
	7T	-631.61421	64	77
PSiH ₂ F (X = F; Y,Z = H)	1	-730.77667	51	2
	2	-730.77770	52	0
	3	-730.72256	49	142
	4S	-730.76738	51	26
	4T	-730.71081	52	176
	5S	-730.70492	49	188
	5T(=6T)	-730.67513	50	267
	6S	-730.70209	48	194
	7S	-730.71168	53	174
	7T	-730.75713	53	55
PSiHF ₂ (X = H; Y,Z = F)	1	-829.84941	37	168
	2	-829.84948	38	168
	3	-829.91423	39	0
	4S	-829.79682	33	302
	4T	-829.77980	34	348
	5S	-829.84407	37	182
	5T(=6T)	-829.80375	39	290
	6S	-829.84794	37	172
	7S	-829.85653	40	152
	7T	-829.90461	40	26
PSiF ₃	1	-928.98167	25	0
	4S	-928.94589	23	92
	4T	-928.90798	23	191
	7S	-928.00631	26	-64
	7T	-929.05465	27	-190

^a See Fig. 1 for definitions of structures and parameters.^b Based on (U)MP2(d,p) geometries, given in Table 3.^c From (U)HF/6-31G(d,p) calculations and scaled by 0.9.Fig. 2. Correlation diagrams showing the relative energy separations (kJ mol⁻¹) of the PCXYZ systems at the QCISD(T)/6-311G(d,p) + ZPE level of theory.

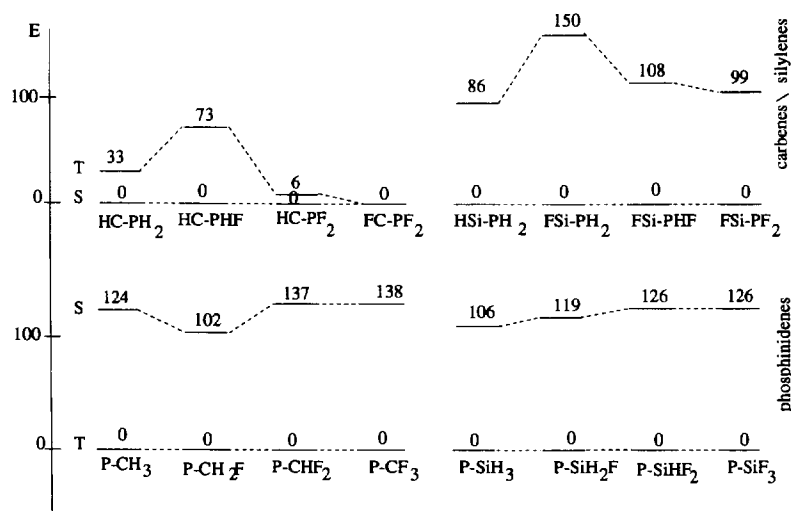


Fig. 3. Correlation diagrams showing the $\Delta E(T-S)$ (kJ mol⁻¹) in phosphinidenes, carbenes and silylenes at the QCISD(T)/6-311G(d,p) + ZPE level of theory.

that, relative to **6S**, the C=P bond of **5S** is shortened by 0.072 Å while the P-F bond becomes 0.010 Å longer. This is caused by a partial charge filling of the anti-bonding $\sigma^*(PF)$ orbital.

The increasing stability of HC-PF₂ **4S** relative to **5S** and **6S**, in contrast to the situation in monosubstitution, can be explained by a geminal interaction of both fluorine atoms which is better known as the 'perfluoro

effect'. This term describes the fact that when two F atoms are in geminal position, they tend to accentuate the stabilization [25]. Again, we identify a sensible structural change in **4S** which is a consequence of the electronic reorganizations: the C-P bond being shortened to 1.577 Å and the HCP angle being widened to 148.5°, thus approaching linearity. Overall, this molecule can be regarded as an alkylidynephosphorane HC≡PF₂.

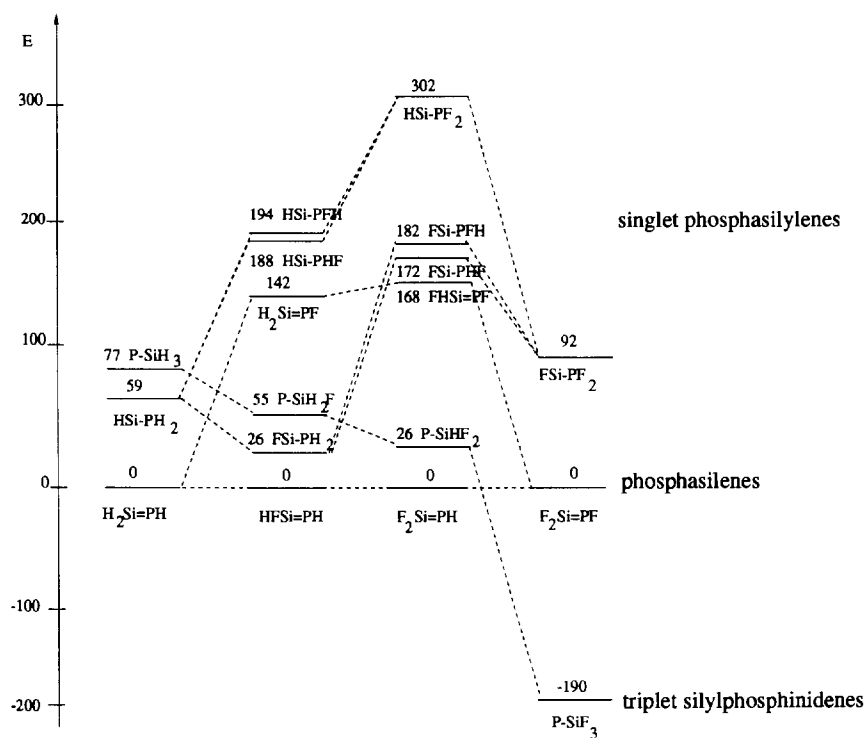


Fig. 4. Correlation diagram for the relative energy separations (kJ mol⁻¹) of the PSiXYZ systems at the QCISD(T)/6-311G(d,p) + ZPE level of theory.

Similar to NPF_2 [11], the electronic structure $\text{HC}\equiv\text{PF}_2$ can be described by different resonance forms shown in Scheme 1. $\text{HC}\equiv\text{PH}^+$ is not a stable form; $\text{H}_2\text{C}=\text{P}^+$ is known to be the most stable protonated form of HCP. Thus, the monosubstituted phosphinocarbene has fewer possibilities for resonance ((A), Scheme 1) making its ionic contributions less important than those arising from the canonical forms of $\text{HC}-\text{PF}_2$ ((B), Scheme 1).

The triplet $\text{P}-\text{CHF}_2$ **7T** remains the more stable phosphinidene. It should be mentioned that, of the PCHF_2 isomers, only $\text{F}_2\text{C}=\text{PH}$ **3** has been generated and characterized by MW, NMR and IR spectroscopies [26–28]. The rotational constants of the latter can be compared as follows:

Calculated	$A_e = 10895$	Experimental	$A_o = 11107$
(MHz):	$B_e = 4726$	(MHz):	$B_o = 4766$
	$C_e = 3296$		$C_o = 3331$

3.1.4. PCF_3 isomers

The energy of phosphoethene $\text{F}_2\text{C}=\text{PF}$ **1** differs from that of $\text{FC}-\text{PF}_2$ **4** by 161 kJ mol^{-1} . Both electronic states of the latter are practically degenerate. Compared with the mono- and disubstituted species, the singlet carbene is destabilized while the triplet is dramatically stabilized. **7S** is further destabilized by the CF_3 group.

3.1.5. Summary

In taking phosphoethylenes $\text{XYC}=\text{PZ}$ as reference molecules (Fig. 2), a few energetic trends can be established as follows.

1. Phosphoethylenes consistently remain the most stable isomers. Within one group of species, the P–F bond strength is the determining reason for the energy difference. Thus $\text{H}_2\text{C}=\text{PF}$, $\text{FHC}=\text{PF}$, $\text{HC}-\text{PHF}$ and $\text{HC}-\text{PF}_2$ are strongly favoured over corresponding F(C)-substituted species. Energetic changes go together with structural reorganizations giving both

$\text{HC}\equiv\text{PFH}$ and $\text{HC}\equiv\text{PF}_2$ an alkylidyne phosphorane character with a formal $\text{C}\equiv\text{P}$ triple bond.

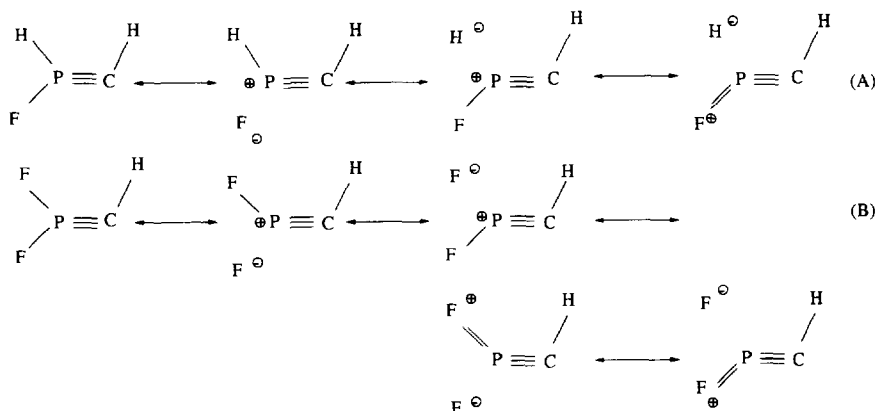
2. While a cis-effect is not operative owing to the long C–P distances, a negative hyperconjugation seems to come into play, either in the CF_2 or in the PF_2 groups, by stabilizing the corresponding structure. In contrast, an anomeric effect is likely to be operative in the difluorosubstituted carbene $\text{FC}-\text{PHF}$, where the *Z*-isomer is actually more stable than the *E*-isomer.
3. In the singlet manifold, the relative position between phosphinocarbenes and methylphosphinidenes is reversed upon fluorination; $\text{HC}-\text{PFH}$, $\text{FC}-\text{PFH}$, $\text{FC}-\text{PF}_2$ becoming now more stable than $\text{P}-\text{CH}_2\text{F}$, $\text{P}-\text{CHF}_2$ and $\text{P}-\text{CF}_3$ respectively.
4. The $\Delta E(\text{T}-\text{S})$ values of phosphinocarbenes are also markedly modified by fluorination. Both electronic states become thus quasi-degenerate in both $\text{HC}-\text{PF}_2$ and $\text{FC}-\text{PF}_2$. Apparently, the PF_2 group stabilizes the triplet carbene much more than the singlet counterpart.
5. The position of singlet phosphinidenes is, relative to their triplets, not significantly displaced upon fluorine substitution. The ground state remains a triplet and the $\Delta E(\text{T}-\text{S})$ varies as follows: -124 kJ mol^{-1} in $\text{P}-\text{CH}_3$, -102 kJ mol^{-1} in $\text{P}-\text{CH}_2\text{F}$, -137 kJ mol^{-1} in $\text{P}-\text{CHF}_2$ and -138 kJ mol^{-1} in $\text{P}-\text{CF}_3$.

3.2. The PSiXYZ isomers

Again, the following discussion is based on phosphasilenes as reference molecules.

3.2.1. PSiH_3 isomers

Contrary to its carbon congeners, phosphasilene **4S** is the second stable isomer (59 kJ mol^{-1} above **1**), followed by the triplet $\text{P}-\text{SiH}_3$ **7T** (77 kJ mol^{-1} above



1). For HSi–PH₂ a singlet–triplet separation of 86 kJ mol⁻¹ has been calculated; this value is not much different from that in SiH₂. The triplet phosphinidene P–SiH₃ **7T** lies slightly higher than the analogous P–CH₃. We note that HSi–PH₂ does have a non-planar structure in line with an earlier study using lower level calculations [19].

3.2.2. PSiH₂F isomers

Monohalogenation results in at least ten different isomers. Both *E*-1 and *Z*-2 forms of silene have similar energies. H₂Si=PF **3**, which consists of a P–F bond, turns out to be much less stable, lying 142 kJ mol⁻¹ above FHSi=PH **2**. Contrary to the carbon–phosphorus species, the P–F bond is no longer a dominating factor of stabilization for the molecule. It rather acts as an electron withdrawer elongating the Si=P bond of **3** to 2.103 Å, while the two others have shorter bond lengths, namely 2.050 Å in **1** and 2.056 Å in **2**. In this case, the competition between both P–F and Si–F bond energies turns in favour of the Si–F by about 75 kJ mol⁻¹ [20]. In the more stable structures **1** and **2**, where there is effectively an Si–F bond, a back-donation of F also occurs, inducing an Si=P bond shortening.

Phosphino-substituted silylenes are, in their turn, influenced by monofluorination at either silicon or phosphorus. Of the three singlet phosphasilylenes, **4S**, having an Si–F bond, is energetically favoured. Compared with the unsubstituted silylene, **4S** is lowered by 33 kJ mol⁻¹. This confirms the interpretation stated above based on the Si–F bond strength. The small energetic preference for *Z*-HSi–PHF **5S** over *E*-HSi–PHF **6S** by 6 kJ mol⁻¹ is again probably due to an anomeric effect. The HSiP fragment adopts a bridged conformation, which is shown by its small angle of 71.0° and 86.4° in **5S** and **6S** respectively. We also note the shorter Si=P bonds (2.083 Å and 2.094 Å) having the same order of magnitude as those of phosphasilylenes **1** and **2**.

The stabilization owing to the $\sigma(\text{SiF})$ bond is also reinforced in the triplet phosphinidene P–SiH₂F **7T**. Even the singlet **7S** now lies much lower in energy than phosphasilylenes **5S** and **6S** in which no Si–F bond is present.

3.2.3. PSiHF₂ isomers

Difluorination enhances the energetic consequences of the duality between Si–F and P–F substitutions. Returning first to the three phosphasilylene structures, F₂Si=PH **3** is largely preferred over FHSi=PF **1** and **2** which lie 168 kJ mol⁻¹ higher in energy. The higher stability of **3** is more easily explained by the strength of two Si–F bonds. Isomers *E*-1 and *Z*-2 are quasi-energetic, confirming the absence of any significant cis-effect. Phosphasilylenes **5S** and **6S**, constructed by an

Si–F bond, are also favoured over HSi–PF₂ **4S** presumably for the same reason as for phosphasilylenes.

The overall effect of difluorine substitution is a strong destabilization of phosphasilylene isomers and a marked stabilization of the triplet phosphinidene PSi–HF₂ **7T** which lies only 26 kJ mol⁻¹ above **3**. Note also an energetic stabilization of **7S** compared with **1** and **2**.

3.2.4. PSiF₃ isomers

The most remarkable result in this perfluorinated system is that the phosphinidene P–SiF₃ **7** becomes now the most stable species in both electronic states. Obviously, this molecule enjoys the presence of three Si–F bonds. The benefit is not merely additive but greatly amplified by a perfluoro effect.

3.2.5. Summary

Schematic correlation diagrams of relative energies are illustrated in Figs. 3 and 4. The following major conclusions can be drawn for the PSiXYZ isomers.

- Both PX₂ and PX moieties become the negative centres. In contrast to their carbon analogues, fluorine substitution at P is no longer a stabilizing factor. When attached to the more electropositive silicon centre, the PX₂ entities show a π -acceptor behaviour resulting in weaker P–Si bonds.
- Fluorine substitution at silicon consistently lowers the energetic content of all different isomeric types, including silenes, silylenes and phosphinidenes. The $\sigma(\text{SiF})$ bond, which is stronger than the $\sigma(\text{PF})$ bond, thus becomes the dominant factor in establishing the energy ordering of this series.
- In going from mono- to difluorine substitution, the Si–F bond strength plays an even more important role. Within the same type of isomer, F₂Si=PH **3** and FSi–PFH **5S** and **6S** are clearly much lower in energy than their isomers.
- Perhalogenation enormously enhances the SiF effect. It is remarkable that the phosphinidene P–SiF₃ **7**, irrespective of its electronic state, turns out to be the global minimum, lying 190 kJ mol⁻¹ below F₂Si=PF. In going from **4S** to **1**, which corresponds to a loss of one P–F bond and a gain of one Si–F bond, structure **1** gains 92 kJ mol⁻¹. Loss of the last P–F bond and gain of an additional Si–F bond which results in **7S**, stabilize the latter by a further energy amount of 64 kJ mol⁻¹.
- Phosphinidenes gain large stabilization when second row substituents are directly attached to the phosphorus atom. Their stability is further enhanced by attachment of fluorine–silicon bonds; the larger the number of F, the greater the stabilization. Thus SiF₃ is more or less the best substituent ever known in stabilizing phosphinidenes in both singlet and triplet states. The $\Delta E(\text{T} - \text{S})$ values in fluorosilylphosphinidenes are in fact not really sensitive to the number of F (Fig. 3).

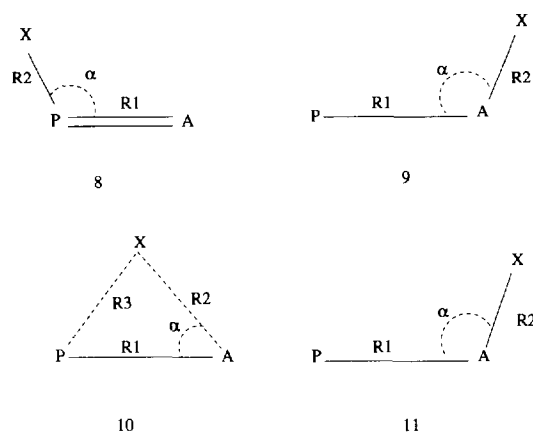


Fig. 5. Schematic representation of PAX equilibrium structures with A = O, S; X = H, F, Cl. Structure **11** is the isomeric triplet phosphinidene. R1, R2, R3 are bond lengths, α is the bond angle.

3.3. POX and PSX isomers

In these systems, we have also considered the chlorine substitution as well as the transition structures connecting the two types of isomer, namely $XP=A$ and $P-AX$. A schematic representation of the PAX molecules considered in which A stands for O or S and X for H, F or Cl is given in Fig. 5. Geometrical parameters, and total and relative energies are recorded in Tables 5 and 6. Structures and energetics of these species obtained by lower level calculations have been reported in earlier studies [29,30].

Table 5
(U)MP2/6-31G(d,p) optimized geometries of XPO, XPS **8**, XOP and XSP **9** and transition structures **10** with X = H, F and Cl; **11** represents the triplet phosphinidene

System ^a	Structure	R1 (Å)	R2 (Å)	R3 (Å)	α (deg)
POH	8	1.517	1.445		105.5
	9	1.643	0.970		110.7
	10	1.569	1.284	1.484	61.8
	11	1.668	0.967		112.4
POF	8	1.486	1.612		110.6
	9	1.494	2.080		110.5
POCl	8	1.506	2.381		116.2
	9	1.521	2.418		98.1
	10	1.949	1.424		102.4
	11	1.982	1.350		107.0
PSH	8	2.067	1.416	1.748	56.6
	9	2.103	1.335		97.3
	10	1.908	1.622		109.4
	11	1.856	1.722		115.9
PSF	8	1.848	2.132	2.512	77.9
	9	2.078	1.657		99.6
	10	1.886	2.066		109.7
	11	1.854	2.419		119.4
PSCl	8	1.874	2.764	3.127	82.4
	9	2.089	2.062		102.7
	10				
	11				

^a See Fig. 5 for definitions.

Table 6

Total and relative energies at the QCISD(T)/6-311G(d,p) level of both POX and PSX systems considered with X = H, F, Cl; relative energies are corrected for ZPEs

System	Structure	Total energy ^a (a.u.)	ZPE ^b (kJ mol ⁻¹)	Relative energy (kJ mol ⁻¹)
POH	8	-416.50976	26	0
	9	-416.45806	34	143
	10	-416.40275	19	274
	11	-416.48717	33	66
POF	8	-515.65293	2	0
	9	-875.62461	13	286
	10	-875.51446	10	316
	11	-875.50231	8	0
PSH	8	-739.11357	23	117
	9	-739.07020	26	206
	10	-739.03170	14	71
	11	-739.08670	23	0
PSF	8	-838.23319	10	219
	9	-838.14916	8	308
	10	-838.11444	6	303
	11	-838.11742	9	0
PSCl	8	-1198.21152	7	149
	9	-1198.15500	8	202
	10	-1198.13416	6	217
	11	-1198.12869	7	

^a Based on (U)MP2/6-31G(d,p) geometries given in Table 5.

^b From UHF/6-31G(d,p) calculations and scaled by 0.9.

3.3.1. POH and PSH isomers

The $HP=O$ and $HP=S$ molecules **8** are more stable than their corresponding singlet phosphinidenes POH **9** and PSH **9** which lie 143 kJ mol^{-1} and 117 kJ mol^{-1} respectively higher on the energy surface. Analogous to silicon-substituted phosphinidenes, we observe here small energy differences for the S species. The energy barrier for unimolecular rearrangement is also smaller for the latter.

3.3.2. POF and PSF isomers

For the POF system, only $FP=O$ could be located. Any attempt to find the isomeric alternatives **9** and **11** failed due to a simple cleavage of the $O-F$ bond, giving the $PO^{\cdot} + F^{\cdot}$ products. Another picture emerges for PSF where four structures could be located. **8** is again the most stable one. Contrary to $P-SH$, the singlet phosphinidene $P-SF$ **9** lies 219 kJ mol^{-1} above **8**, which corresponds to an increase of about 100 kJ mol^{-1} in energy difference; this is mainly due to the existence of a very strong $P-F$ bond in $FP=S$. The effect of fluorine on phosphinidene is an ordering reversal between singlet and triplet states. The singlet state **9** now becomes the ground state and gains 84 kJ mol^{-1} relative to the triplet **11**.

In the singlet phosphinidene, the 1,2 F-shift demands an energy barrier of 89 kJ mol^{-1} , a value close to that for the 1,2-H shift in $P-SH$.

3.3.3. POCl and PSCl system

Contrary to the POF system, chlorine substitution gives rise to three distinct isomers, where the most stable one is CIP=O **8**. The singlet phosphinidene **9** exists, but differs from **8** by a noticeably larger energy amount of 286 kJ mol^{-1} . Despite several efforts, we could not find the transition structure **10** connecting **8** with **9**. Both species are thus connected by their dissociation limit $\text{PO} + \text{Cl}$. Again, the singlet becomes the ground state of P–OCl and P–SCl, with a smaller energy gap for the P–SCl system. For the CIPS system, we can easily locate a transition structure **10** for 1,2-Cl shift which only demands an activation energy of 53 kJ mol^{-1} starting from **9**.

4. Conclusion

We have focused in this theoretical study on the relative energies between the double bond species featuring phosphorus $\text{XP}=\text{CX}_2$, $\text{XP}=\text{SiX}_2$, $\text{XP}=\text{O}$, $\text{XP}=\text{S}$ and their rearranged products $\text{XC}-\text{PX}_2$, $\text{P}-\text{CX}_3$, $\text{XSi}-\text{PX}_2$, $\text{P}-\text{SiX}_3$, $\text{P}-\text{OX}$ and $\text{P}-\text{SX}$. We do not intend to repeat here the conclusions drawn after each section, but rather to make a link between the carbon, silicon, oxygen and sulphur systems.

In general, when a phosphorus atom is bonded to a more electronegative element such as carbon, oxygen and sulphur, halogenation, and in particular fluorination, at P enormously stabilizes this species. The relative stability of possible isomers is overwhelmingly dominated by the strength of the P–F bond. When P is bonded to more electropositive elements, such as Si, a reversal of role occurs. The competition between both halogen–silicon and halogen–phosphorus bonds turns out to be in favour of the silicon. Thus, in SiP systems, the relative energies are mainly determined by the presence of Si–F bonds. Perfluorination amplifies the effect in such a way that, in the PSiX_3 system, the P–SiF₃ phosphinidene becomes the most stable isomer, making it an attractive target for a laboratory preparation. The Si–F bond strength largely compensates for the inherent instability of phosphinidene.

In some cases, negative hyperconjugation effects (i.e. $n(\text{C}) \rightarrow \sigma^*(\text{PF})$) play a noticeable role, whereas the cis-effect is not present at all. The lone pair in the XYPX_2 types ($\text{Y} = \text{C}$ or Si) induces an energy stabilization via an anomeric effect $n(\text{C or Si}) \rightarrow \sigma^*(\text{PF})$ in difluorinated phosphacarbene or phosphasilylenes which overall favours the Z-isomer.

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